

Title (en)
Process for the preparation of aromatic olefines by catalysis of palladacycles

Title (de)
Verfahren zur Herstellung von aromatischen Olefinen unter Katalyse von Palladacyclen

Title (fr)
Procédé de fabrication d'oléfines aromatiques par catalyse de paladacycles

Publication
EP 0688757 A1 19951227 (DE)

Application
EP 95109414 A 19950619

Priority
DE 4421730 A 19940622

Abstract (en)
Process for prepn. of olefin-substd. aromatic cpds. of formula (I), in which R1a to R5a independently=H, 1-8C alkyl, 1-8C alkoxy, 1-8C acyloxy, O-phenyl, F, Cl, OH, NO2, CN, COOH, CHO, SO3H, SO2R, SOR, NH2, NH(1-8C alkyl), N(1-8C alkyl)2, C(Hal)3, NHCO-(1-4C alkyl), N-(1-4C alkyl)-CO-(1-4C alkyl), COO-(1-8C alkyl), CONH2, CO-(1-8C alkyl), NHCOH, NCOO-(1-4C alkyl), CO-phenyl, COO-phenyl, CHCHCO2-(1-8C alkyl), CHCHCO2H, PO-(phenyl)2 or PO-(1-4C alkyl)2 and one gp. R1a to R5a may also be a gp. of formula -(R6a)C=C(R7a)R8a; R6a=H, 1-8C alkyl, phenyl, O-(1-8C alkyl) or F and R7a and R8a independently=CN, COOH, CO2-(1-8C alkyl), CONH2, CONH-(1-4C alkyl), CON(1-4C alkyl)2, F, CO2-phenyl, H, alkyl, phenyl, PO(phenyl), PO(1-4C alkyl)2, CO-phenyl, CO-(1-4C alkyl), O-(1-4C alkyl), NH-(1-4C alkyl), PO3H, SO3H, SO3-(1-4C alkyl), SO2-(1-4C alkyl) or O-phenyl, comprises reacting haloaromatic cpds. of formula (II) with olefins of formula (III), in which R1a to R8a are as above and one of the gps. R1a to R5a may also=X, and X=Br, I, Cl, OSO2CF3, OSO2-phenyl or OSO2CH3, in the presence of a palladium cpd. catalyst of formula (IV), in which R<1>, R<2>, R<3>, R<4>, R<5> and R<6> independently =H, 5-8C cycloalkyl, 1-4C alkyl, 1-4C alkoxy, F, NH2, NH-(1-4C alkyl), N(1-4C alkyl)2, CO2(1-4C alkyl), OCO(1-4C alkyl) or phenyl or R<1> and R<2>, R<2> and R<3>, R<3> and R<4> or R<5> and R<6> may together complete an aliphatic or aromatic ring, R<7> and R<8>=1-8C alkyl, 3-12C cycloalkyl, or opt. substd. aryl gp., and Y=an anion of an (in)organic acid, and conducting the reaction in the presence of a dipolar aprotic solvent and a base at temps. of 20-200 deg.C.

Abstract (de)
Die Erfindung betrifft ein Verfahren zur Herstellung von monofunktionellen, bi- und polyfunktionellen aromatischen Olefinen der Formel (I) <IMAGE> worin R<1a> bis R<5a> unabhängig voneinander Wasserstoff, C1-C8-Alkyl, Alkoxy-(C1-C8), Acyloxy-(C1-C8), OPhenyl, Phenyl, Fluor, Chlor, Brom, Iod, OH, NO2, OSO2CF3, CN, COOH, CHO, SO3H, SO2R, SOR, NH2, NHAlkyl (C1-C8), N-Alkyl2-(C1-C8), CHal3, NHCO-Alkyl-(C1-C4), N-Alkyl-(C1-C4)-CO-Alkyl-(C1-C4), COO-Alkyl-(C1-C8), CONH2, CO-Alkyl-(C1-C8), NHCOH, NCOO-Alkyl-(C1-C4), CO-Phenyl, COO-Phenyl, CHCH-CO2Alkyl-(C1-C8), CHCHCO2H, PO-Phenyl2, PO-Alkyl2-(C1-C4), wobei einer der Reste R<1a> bis R<5a> auch <IMAGE> darstellen kann, R<6a> Wasserstoff, Alkyl(C1-C8), Phenyl, O-Alkyl-(C1-C8), Fluor R<7a> und R<8a> unabhängig voneinander Wasserstoff, CN, CO2H, CO2-Alkyl-(C1-C8), CONH2, CONH-Alkyl-(C1-C4), CON(Alkyl)2-(C1-C4), Fluor, CO2-Phenyl, Alkyl, (C1-C8)-Phenyl, PO(Phenyl), PO(Alkyl-(C1-C4))2, CO-Phenyl, CO-Alkyl-(C1-C4), O-Alkyl-(C1-C4), NH-Alkyl-(C1-C4), PO3H, SO3H, SO3-Alkyl-(C1-C4), SO2-Alkyl-(C1-C4), O-Phenyl, bedeuten, durch Umsetzung von Halogenaromaten der allgemeinen Formel (II) <IMAGE> mit Olefinen der allgemeinen Formel (III) <IMAGE> worin R<1a> bis R<8a> die angegebene Bedeutung besitzen, wobei einer der Reste R<1a> bis R<5a> auch für X stehen kann und X Iod, Brom, Chlor, OSO2CF3, OSO2Phenyl, OSO2CH3 bedeutet, dadurch gekennzeichnet, daß man als Katalysator eine Palladiumverbindung der allgemeinen Formel (IV) <IMAGE> worin R1, R2, R3, R<4>, R<5>, R<6> unabhängig voneinander Wasserstoff, (C1-C4)-Alkyl, (C5-C8)-Cycloalkyl, (C1-C4)-Alkoxy, Fluor, NH2, NH-Alkyl(C1-C4), N(Alkyl)2-(C1-C4), CO2Alkyl-(C1-C4), OCO-Alkyl-(C1-C4), oder Phenyl bedeuten, oder R1 und R2, R2 und R3, R3 und R<4>, R<5> und R<6> zusammen einen aliphatischen oder aromatischen Ring bilden, und R<7>, R<8> (C1-C8)-Alkyl, (C3-C12)-Cycloalkyl, substituiertes oder unsubstituiertes Aryl sind Y ein Anion einer anorganischen oder organischen Säure bedeutet, einsetzt.

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